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Novel Light-Emitting Devices Based on Pyridine-Containing Conjugated Polymers

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13. ABSTRACT (Maximum 200 words)

We present novel light-emitting devices based on several pyridine-containing conjugated polymers and copolymers in various device configurations. The high electron affinity of pyridine-based polymers improves stability and electron transport properties of the polymers and enables the use of relatively stable metal such as AL as electron injecting contacts. Bilayer devices utilizing poly (9-vinyl carbazole) (PVK) as hole transporting/electron blocking polymer show dramatically improved efficiency and brightness as compared to single layer devices, which is attributed to charge confinement and exciplex emission at the PVK/emitting polymer interface. The incorporation of conducting polyaniline network electrode top PVK reduces the device turn-on voltage significantly while maintaining the high efficiency. Novel device configurations such as inverted light-emitting devices and symmetrically configured AC light-emitting (SCALE) devices enable the use of ITO as electron injecting contact, eliminating the use of low workfunction metals as electrodes, potentially improving the device operating stability and shelf lifetime.

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Novel light-emitting devices based on pyridine-containing conjugated polymers

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Abstract

We present novel light-emitting devices based on several pyridine-containing conjugated polymers and copolymers in various device configurations. The high electron affinity of pyridine-based polymers improves stability and electron transport properties of the polymers and enables the use of relatively stable metal such as Al as electron injecting contacts. Bilayer devices utilizing poly(9-vinyl carbazole) (PVK) as hole transporting/electron blocking polymer show dramatically improved efficiency and brightness as compared to single layer devices, which is attributed to charge confinement and exciplex emission at the PVK/emitting polymer interface. The incorporation of conducting polyaniline network electrode to PVK reduces the device turn on voltage significantly while maintaining the high efficiency. Novel device configurations such as inverted light-emitting devices and symmetrically configured AC light-emitting (SCALE) devices enable the use of ITO as electron

injecting contact, eliminating the use of low workfunction metals as electrodes, potentially improving the device operating stability and shelf lifetime.

I. INTRODUCTION

Since its discovery in 1990 in poly(p-phenylene vinylene) (PPV) [1], conjugated polymer electroluminescence (EL) has been considered an important property with many potential applications. Electroluminescence combined with other unique properties of polymers, such as processibility, band gap tunability, and mechanical flexibility, make conjugated polymers excellent candidates for low cost large area display applications. In addition to PPV, a variety of PPV derivatives and other conjugated polymers and copolymers have been found to exhibit electroluminescent properties [2,3]. Light-emitting devices incorporating these materials have demonstrated all the necessary colors needed for display applications.

The device performance has been improved dramatically since the initial fabrication A number of techniques have been developed to improve the device performance. One way is to use low workfunction metal, such as Ca, as electron injecting electrode (cathode) [?]. The double charge injection mechanism of polymer light-emitting diodes (LEDs) requires the match of cathode (anode) workfunction to the corresponding LUMO (HOMO) level of the polymer in order to achieve efficient charge injection. The relatively small electron affinity of most conjugated polymers requires metals with very low workfunctions to achieve efficient electron injection. However, since low workfunction metals are generally oxygen reactive, devices with low workfunction cathode are usually unstable. Thus, polymers with high electron affinities are highly desirable.

Pyridine-based conjugated polymers have been shown to be promising candidates for light-emitting devices [5,6] due to their high electron affinity. As compared to phenylene-based analogues, the pyridine-based polymers are more resistant to oxidation and show better electron transport properties. Figure 1 shows the structures of the pyridine-containing polymers and copolymers, namely poly(p-pyridine) (PPy), poly(p-pyridyl vinylene) (PPyV),

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and copolymers of PPyV and PPV (PPyVP(R)$_2$V) with various functional sidegroups R = C$_{12}$H$_{25}$, OC$_{16}$H$_{33}$, COOC$_{12}$H$_{25}$. With respect to π electronic levels, $-$C$_{12}$H$_{25}$ is slightly electron donating; $-$OC$_{16}$H$_{33}$ electron donating; and $-$COOC$_{12}$H$_{25}$ electron withdrawing. The pyridine-based polymers are highly luminescent, especially the copolymers. The internal photoluminescent quantum efficiency of the copolymers have been measured [7] under ambient environment to be 75-90% in solution and 18-30% in film, with the exception of the $-$OC$_{16}$H$_{33}$ copolymer. The electron donating nature of $-$OC$_{16}$H$_{33}$ makes the copolymer more susceptible for oxidation. As a result, the PL quantum efficiency of the $-$OC$_{16}$H$_{33}$ copolymer is only 2% in film although it is high (80%) in solution. To reduce the oxidation effects, the strapped copolymer (@PPyVPV) was introduced, as shown in Fig. 1 (d). Also the strapped copolymer shows less aggregation effect as compare to the "usual" copolymers (see below).

Another common technique to improve device performance is to incorporate charge transporting layers in a multilayer device structure. The charge transporting layer enhances the transport of one type of charge while blocking the other, achieving balanced charge injection and transport and spatially confines emission zone away from electrode, avoiding nonradiative quenching effects near electrodes. To date the highest efficiency polymer light-emitting devices reported are multilayer devices [8].

Here we present light-emitting devices based on the pyridine-containing polymers and copolymers in various device configurations. The high electron affinity of pyridine based polymers enables the use of relatively stable conductors such as Al as electron injecting contacts. Taking advantages of the better electron transport properties of the pyridine-containing polymers, we fabricate bilayer devices utilizing poly(9-vinyl carbazole) (PVK) as hole transporting/electron blocking polymer, which improves the device efficiency and brightness significantly due to the charge confinement and exciplex emission at the PVK/emitting polymer interface. The incorporation of conducting polyaniline network electrode to PVK reduces the device turn on voltage significantly while maintaining the high efficiency. The high electron affinity of the pyridine-based polymers enables the use of ITO

as electron injecting contact to fabricate inverted light-emitting devices [9]in which ITO and Au were used as cathode and anode, respectively. By inserting an "insulating" layer on both side of the emitting polymer, we fabricated symmetrically configured AC light-emitting (SCALE) devices [6]which work under both forward and reverse DC bias as well as in AC modes. Both the inverted and the SCALE devices are capable of eliminating the use of low workfunction metals as electrodes, potentially improving the device operating stability and shelf lifetime.

II. EXPERIMENT

The synthesis of the pyridine-containing polymers has been reported earlier [10–12]. For single layer devices, the emitting layer was spin-cast from solutions in formic acid (for PPy and PPyV) or xylenes (for copolymers) (with a concentration 10 mg/ml) onto pre-cleaned patterned ITO substrates with sheet resistance of 15 Ω/square at 1000-2000 rpm. For bilayer devices, PVK layer was spin coated onto ITO substrate from solution in tetrahydrofuran (THF) (10 mg/ml) at $\sim$ 3000 rpm. The emitting layer was then spin coated on top of the PVK layer from appropriate solutions. The conducting polyaniline network electrode was formed by spin-cast blend of camphor sulfonic acid doped polyaniline (PAN-CSA) and low molecular weight host polymer poly(methyl methacrylate) (PMMA) (from Aldrich Chemical Co.) in an appropriate ratio in m-cresol. The host polymer PMMA was subsequently washed away by xylenes. The PVK and emitting layers were similarly coated as in the bilayer device. All solutions were filtered using Gelman Acrodisc CR PTFE 1μm filters. The top metal electrode was deposited by vacuum evaporation at a pressure below 10^{-6} torr. To prevent damage to the polymers, the substrate was mounted on a cold-water cooled surface during evaporation. Figure 2 shows schematically the structure of a bilayer device with PAN-CSA network electrode (N. E.).

Absorption spectra were measured on spin-cast films using a Perkin-Elmer Lambda 19 UV/VIS/NIR spectrometer. Photoluminescence (PL) and EL were measured using a PTI

fluorometer (model QM-1). The current-voltage (I-V) characteristics were measured simultaneously with EL using two Keithley 195A multimeters while dc voltage was applied by a HP 6218A DC power supply. Quantum efficiency and brightness were measured using a calibrated photodiode (UDT UV100).

III. RESULTS AND DISCUSSION

Figure 3 compares the electroluminescence-voltage (EL-V) and electroluminescence-current (EL-I) characteristics for a single layer device, a bilayer device, and a bilayer device with PAN-CSA network electrode using the ε rapped copolymer as emitting layer. As compared to those of the single layer device, the quantum efficiency of the bilayer device increase more than two orders of magnitude. reaching 0.3%. The brightness of the bilayer device follows closely with the current density, reaching ~ 50 cd/m^2 at ~ 0.2 mA/mm^2 (~ 22 V) and ~ 300 cd/m^2 at ~ 2 mA/mm^2 (~ 27 V). PVK is a well known hole transporting/electron blocking polymer. Besides the function of enhancing the transport of holes injected from anode, it blocks the transport of electrons injected from cathode such that the electrons accumulate at the PVK/copolymer interface. This greatly enhance the probability of radiative recombination. In addition, the PVK layer separates the recombination zone from the metal electrode so that the radiative recombination is protected against the well known non-radiative quenching at the metal/polymer interfaces.

One side effect of using the PVK layer is that it increases the device operating voltage substantially. One effective way to reduce the device turn on voltage is to use high surface network electrode [13]. The concept behind the network electrode is that a rough electrode will create a non-uniform high electric field that enhances the charge injection. This technique has been successfully applied to PPV based devices [13]. By applying this technique to the PVK layer, the device operating voltage decreased significantly. For the devices shown here, the device operating voltage reduced significantly (see Fig. 3 (a)). The brightness of the bilayer device with network electrode reaches ~ 50 cd/m^2 at only ~ 9 V,

instead of ~ 22 V for bilayer devices without network electrode. Since the incorporation of the PAN-CSA network electrode does not modify the PVK/copolymer interface, the high quantum efficiency and brightness of the bilayer device are maintained (see Fig. 3 (b)). Thus, the incorporation of the network electrode to the bilayer device improves the power efficiency dramatically. The bilayer devices with and without PAN-CSA network electrode show similar EL spectra, which are blue shifted as compared to that of the single layer device, see Fig. 4. The slightly reduced intensity at high energy tail for the device with network electrode is probably due to absorption of PAN-CSA.

The species that responsible for the light generation in the bilayer device is attributed to exciplexes formed at the PVK/copolymer interface, and is identified by the PL measurements. Figure 5 compares the PL of pure copolymers, pure PVK, and bilayer of PVK/copolymer. The PL of PVK film (open circles) excited at 3.6 eV show an emission peak at 3.06 eV, agree well with the value reported in the literature [14,15]. The PL of the coplymers with R = $C_{12}H_{25}$ and COO $C_{12}H_{25}$ peaks at ~ 2.15 eV and ~ 2.03 eV, respectively. In contrast, the PL of strapped copolymer film shows a shoulder at 2.25 eV, in addition to the main peak at ~ 2.03 eV. The peak of the film PL is clearly red-shifted as compare to solution PL for all the copolymers, which has been attributed to the aggregate formation in the film [16].

The solid lines in Fig. 5 are the PL spectra for the PVK/copolymer bilayer films excited at 3.6 eV, an energy that is greater than the band gap of PVK. In each case, more prominently in Fig. 5 (b) and (c), there is PL emission at the same energy as the PVK PL emission (3.1 eV). However, the main feature in the PL of the bilayer films is located at 2.5 eV for the copolymers with R = $C_{12}H_{25}$ and $COOC_{12}H_{25}$ and 2.4 eV for the strapped copolymer. Emission at these energies is not observed for individual films of either PVK or the copolymers indicating that the emission is due to a completely different species, and is attributed to the exciplex. When the excitation energy is lowered below 3.4 eV (band gap of PVK) the emission due to the exciplex is drastically reduced. In addition, varying the concentration or thickness of the copolymer or PVK films in the bilayer configuration will

change the relative strengths of the exciplex peak and PVK peak.

The assignment of exciplex emission is supported by the optical absorption and photoluminescence excitation (PLE) measurements. Fig. 6 shows the optical absorbance for the single and bilayer systems. Each of the plots shows the absorbance of a single layer of PVK, a single layer of the copolymer, and the bilayer PVK/coplymer films. The onset of PVK absorption is at 3.5 eV and shows two spectral features at 3.6 and 3.75 eV similar to previous reports [14,15]. The absorbance of the bilayer film in each case is the sum of that of each individual component. No new ground to excited state transitions are present. Same results are found for the photoluminescence excitation (PLE) measurements (not shown). As expected, exciplexes do not form when both species are in unexcited states.

We note that a shoulder at 2.2 eV appears in both single and bilayer PL for the strapped copolymer. Although the strapped and the corresponding unstrapped copolymer show similar features in solution PL, no shoulder was found in the film PL for the unstrapped copolymer. We attribute the shoulder to the partial break of the aggregate formation due to the wrap-around of the $C_{10}H_{20}$ chains. This assignment is supported by the PL measurements of the blends of the strapped copolymer in PMMA. When the concentration of the strapped copolymer decreases, the strength of the shoulder grows and blue shifted towards the solution PL, eventually becomes the dominant feature, indicating that the PL is dominated by unaggregated sites in the blend. The same shoulder also appears in the bilayer film of PVK/strapped copolymer indicating that in addition to exciplex, unaggregated sites of pure strapped copolymer also contribute to the PL of the bilayer film. The EL of the PVK/strapped copolymer bilayer device follows closely with the PL of the bilayer film suggesting that a both the exciplex and unaggregated sites of pure strapped copolymer contribute to the light generation unlike the case of other "regular" coplymers in which exciplex is responsible entirely for EL emision.

The high electron affinity of the pyridine-based polymers enables novel device configurations such as inverted light-emitting devices [9] that are capable of eliminating the use of low workfunction metals. Poly(p-pyridine) (PPy) has an electron affinity of ~ 3.5 eV

[17], which allows metals with relatively high workfunction as electron injecting contact. In the inverted light-emitting devices, ITO was used as electron injecting contacts, unlike most polymer LEDs which use ITO as hole injecting contacts. Au, a metal with even higher workfunction, was used as hole injecting electrode. The inverted $(-)$ITO/PPy/Au$(+)$ device show improved device performance including quantum efficiency, brightness, operating stability and storage lifetimes as compared to the usual $(+)$ITO/PPy/Al$(-)$ device. By inserting a PVK layer in between the PPy and Au, the device performance improves further. Figure 7 shows the I-V characteristics of an $(-)$ITO/PPy/PVK/Au$(+)$ device. The device has a typical turn on voltage of $\sim$ 10 V, and light follows closely with current after turn on. The device structure is shown schematically in Fig. 7 inset.

Other novel device configurations such as SCALE (symmetrically configured AC light-emitting) devices [6]also allows the elimination of low workfunction metals as electrodes. The SCALE devices consist of an active emitting layer sandwiched between two "insulating" polymer layers which are able to accept both electrons and holes. This configuration enables the SCALE devices to work under both forward and reverse DC bias. Due to the relatively fast dynamic response, the devices can also be operated in AC modes. This unusual behavior is attributed to the effects of charge accumulation at the emitting polymer/insulating polymer interfaces.

IV. CONCLUSION

In summary, pyridine containing conjugated polymers and copolymers are excellent candidates for polymer light-emitting devices. The high electron affinity of pyridine based polymers enables the use of relatively stable metals such as Al as efficient electron injecting contacts. Taking advantages of the better electron transport properties of the pyridine-containing polymers, we fabricate bilayer devices utilizing PVK as hole transporting/electron blocking polymer. The bilayer device structure improves the device quantum efficiency and brightness significantly due to the charge confinement and the exciplex emission at the

PVK/emitting polymer interface. The incorporation of the conducting polyaniline network electrode to PVK reduces the device turn on voltage significantly while maintaining the high efficiency and brightness of the bilayer device. The high electron affinity of the pyridine-based polymers enables the fabrication of novel devices such inverted light emitting devices and SCALE devices which are capable of eliminating the use of low workfunction metals as electrodes, potentially improving the device operating stability and shelf lifetime.

V. ACKNOWLEDGMENT

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FIGURES

FIG. 1. Structures of pyridine based conjugated polymers and copolymers: (a) poly(p-pyridine) (PPy), (b) poly(p-pyridyl vinylene) (PPyV), (c) copolymers of PPyV and PPV derivatives $(PPyVP(R)_2V)$ with various functional sidegroups R = $C_{12}H_{25}$, $OC_{16}H_{33}$, $COOC_{12}H_{25}$., and (d) strapped copolymer (@PPyVPV).

FIG. 2. Schematic structure of a bilayer device with conducting polyaniline network electrode.

FIG. 3. Comparison of (a) light-voltage and (b) light-current characteristics for a single layer device (square), a bilayer device (circle), and a bilayer device with PAN-CSA network (triangle).

FIG. 4. Normalized EL spectra of the single layer device (dashed line), the bilayer device (solid line), and the bilayer device with network electrode (dash-dotted line).

FIG. 5. Photoluminescence of (a) $PPyVP(C_{12}H_{25})_2V$ film (dashed line), $PVK/PPyVP(C_{12}H_{25})_2V$ bilayer film (solid line), PVK film (circle), (b) $PPyVP(COOC_{12}H_{25})_2V$ film (dashed line), $PVK/ PPyVP(C_{12}H_{25})_2V$ bilayer film (solid line), PVK film (circle), and (c) strapped copolymer.film (dashed line), PVK/strapped copolymer bilayer film (solid line), PVK film (circle).

FIG. 6. Absorbance of a single layer of PVK, a single layer of copolymer, and a bilayer of PVK/copolymer. (a) $PPyVP(COOC_{12}H_{25})_2V$, (b) $PPyVP(C_{12}H_{25})_2V$ and (c) strapped copolymer.
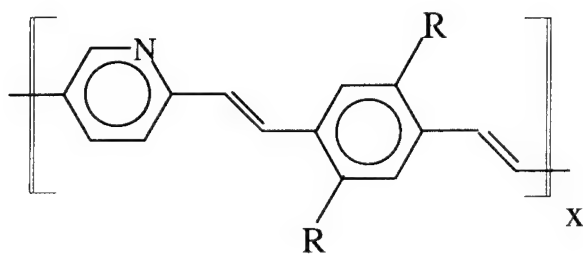
FIG. 7. Current-voltage characteristics of an inverted light-emitting devices with PPy as emitting layer and PVK as hole transporting layer. Inset: schematic device structure of such an inverted device
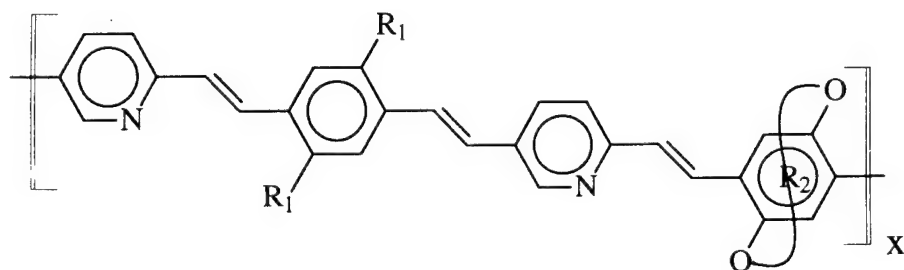
(a)

(b)

$R = C_{12}H_{25}, \ COOC_{12}H_{25}, \ OC_{16}H_{33}$

(c)

$R_1 = OC_{16}H_{33,} \quad R_2 = (CH_2)_{10}$
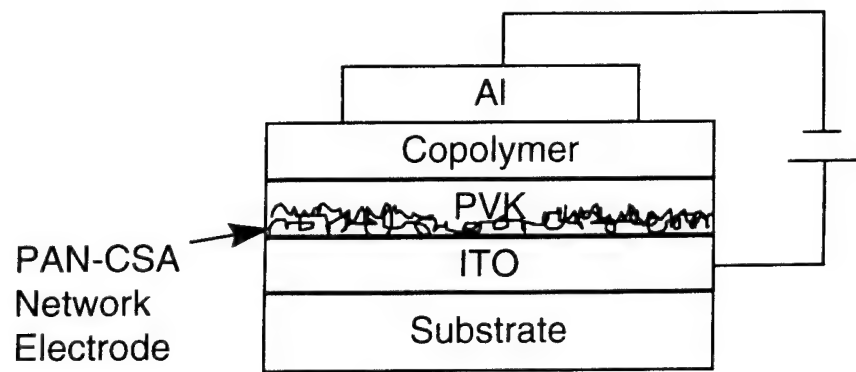
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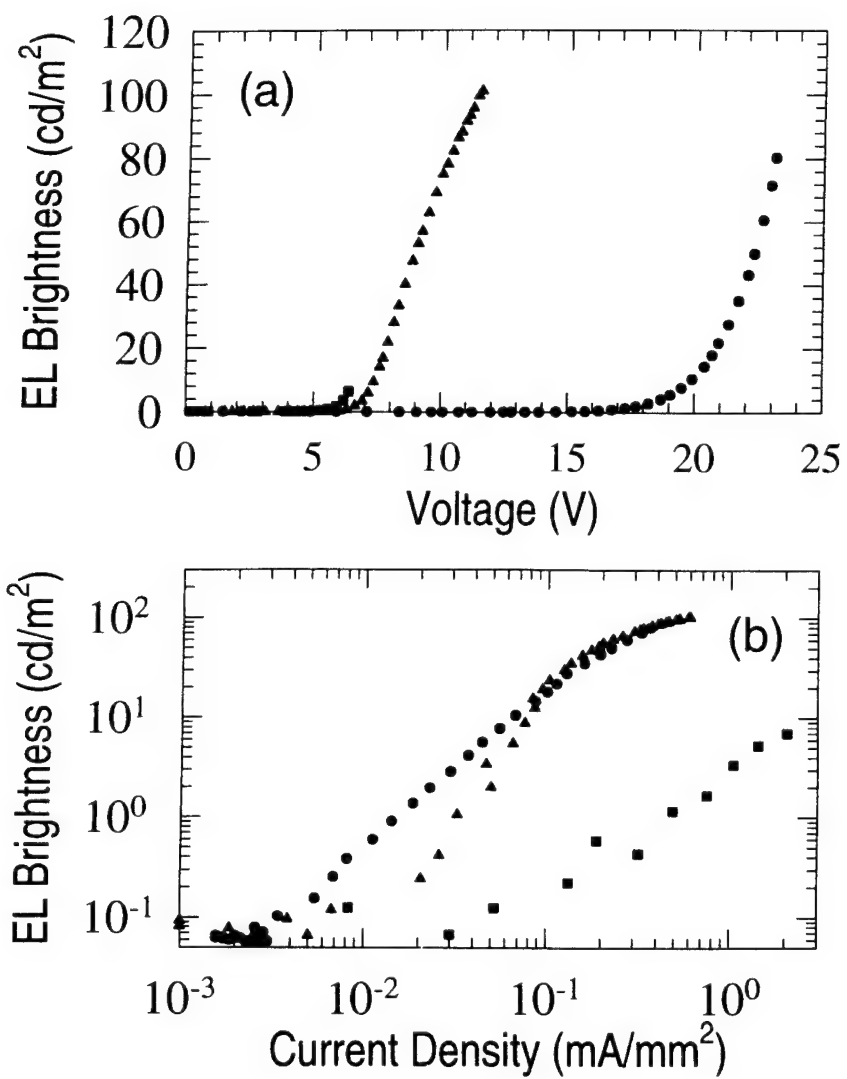Fig. 1 Wang et al.

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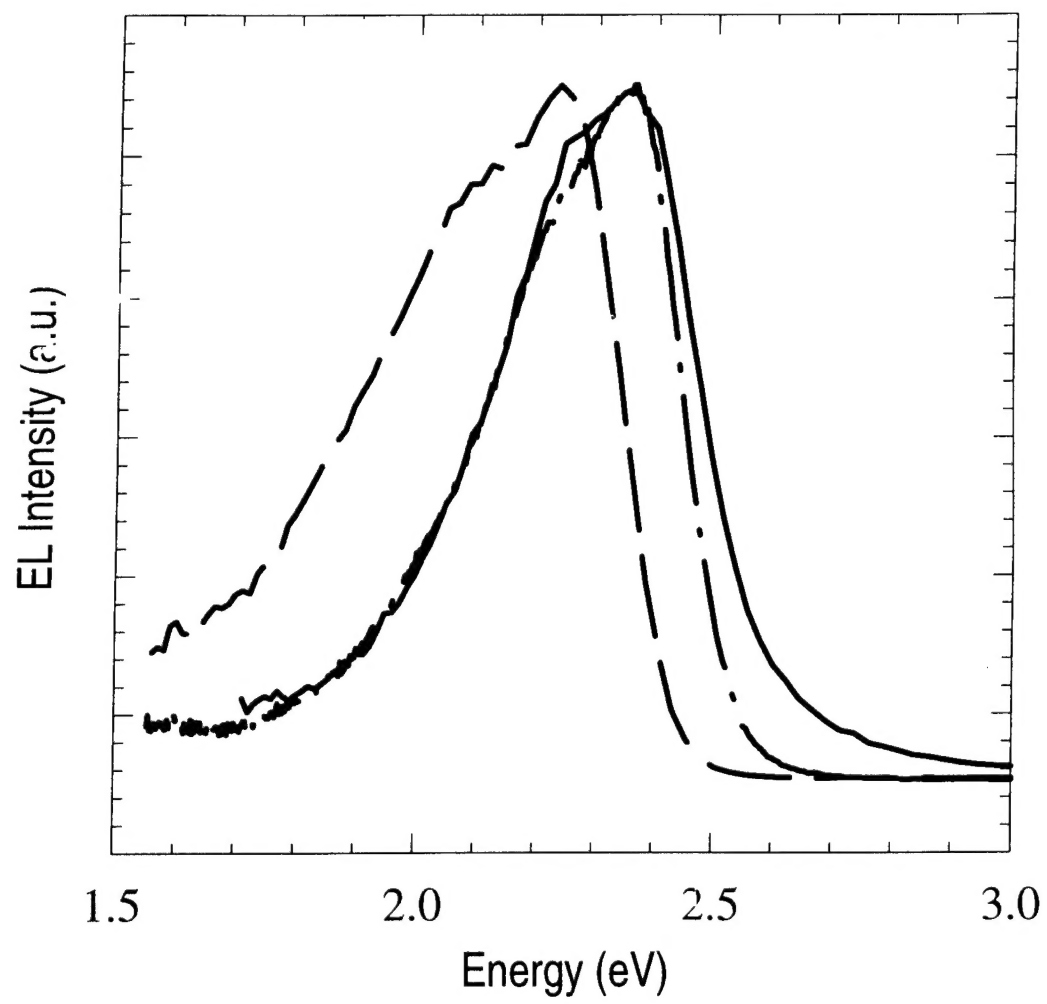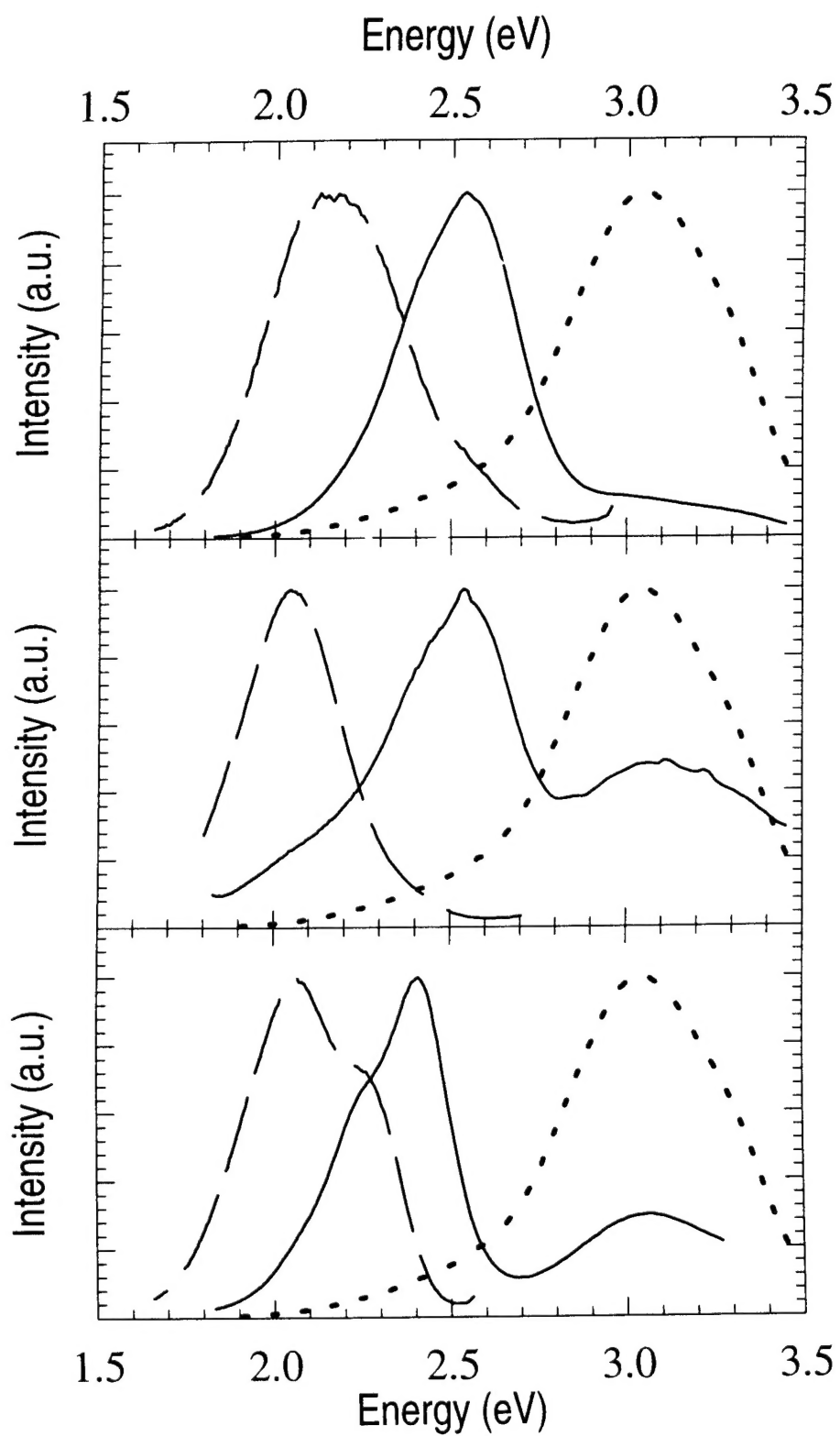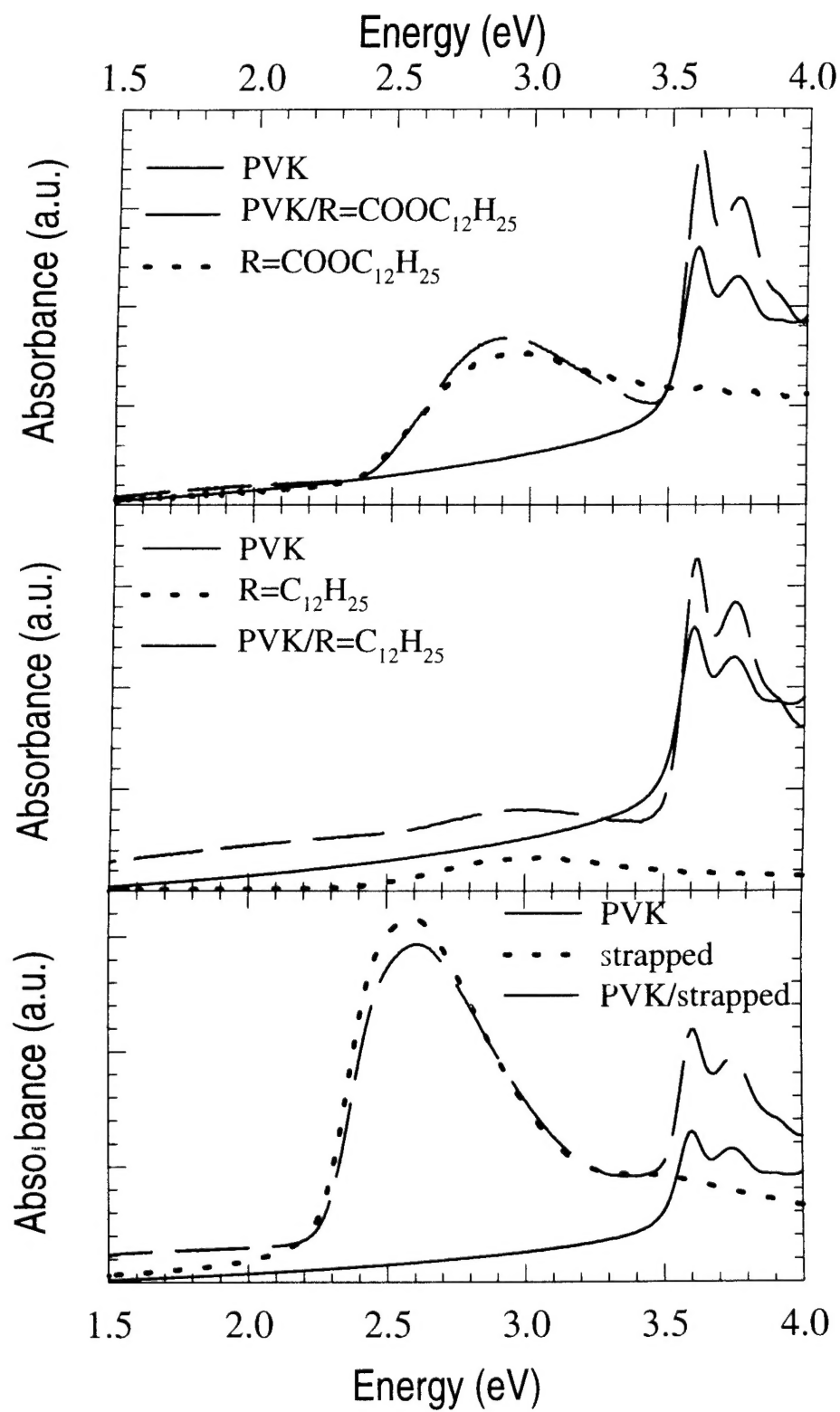
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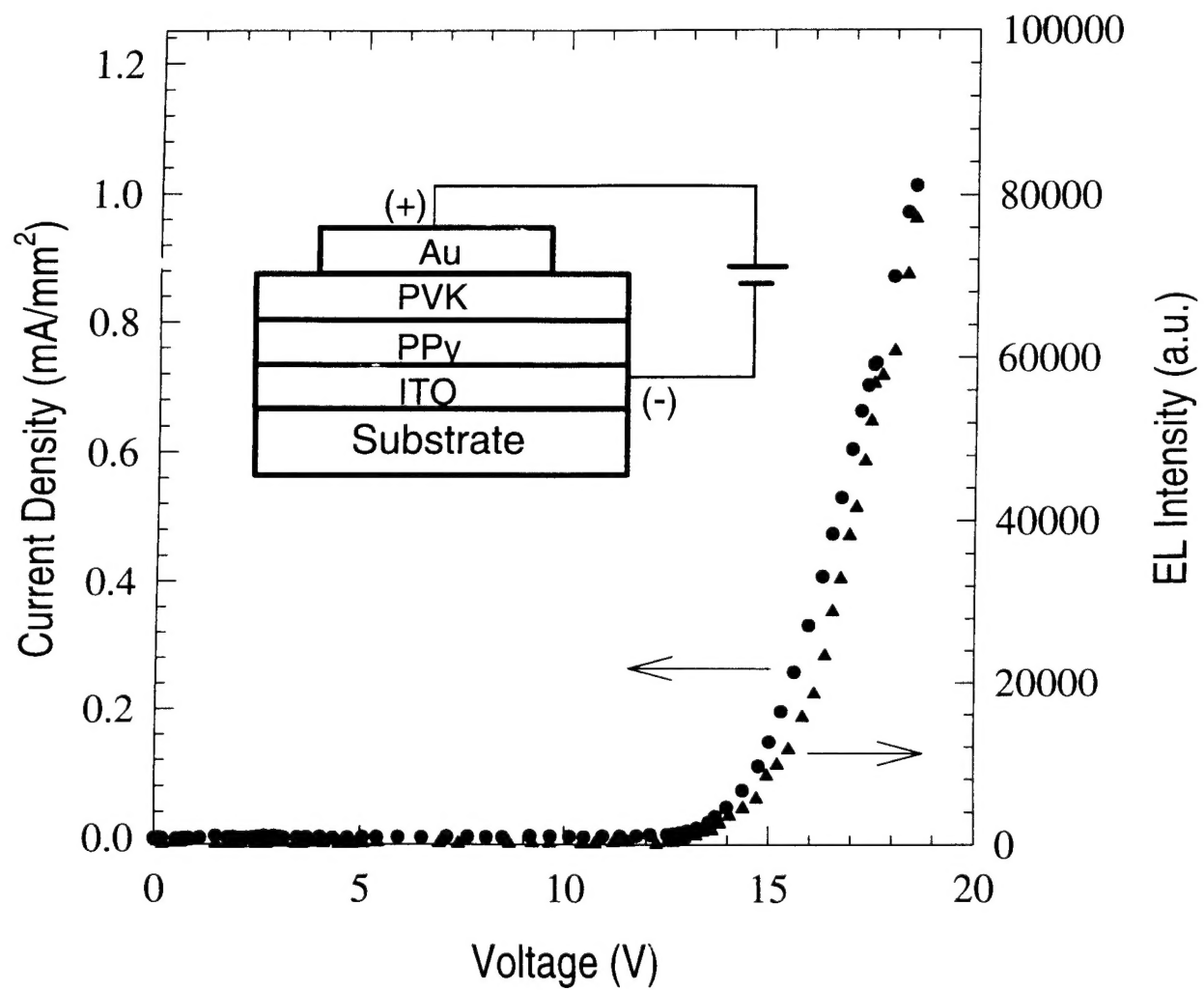
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Fig. 5 Wang et al.

Fig. 6 Wang et al.

Fig. 7 Wang et al.